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# NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1305

ON IONIZATION AND LUMINESCENCE IN FLAMES

By E. Sänger<sup>Eugen</sup>, P. Goercke, and I. Bredt<sup>rene</sup>

Translation of "Über Ionisierung und Lumineszenz in Flammen."  
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I. STATEMENT OF THE PROBLEM

The values found in measuring the reflection and absorption power of the exhaust gas jets of rockets with electric waves (reference 1) can be explained only by a combustion gas ionization higher by many powers of ten than that resulting from the usual equilibrium calculation, for instance, according to the Saha equation.

In big rockets, 80 to 350 kg liquid fuels per second are prepared for combustion. The heat quantities required merely for evaporizing such fuel quantities and heating them up until ignition are of the order of magnitude of 20,000 to 100,000 kcal/sec. Only a few tenths of a percent of this energy transfer may be explained by convection and thermal gas radiation (references 2 and 3). The presumable source of the extraordinary additional heat sources that obviously are present is the phenomenon of chemiluminescence (glow produced by chemical action).

After a brief reference to the determination of the degree of ionization from reflection measurements and its calculation according to the Saha equation, we shall attempt in the following sections to give an explanation for the great difference in the results of measurements

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and calculation, taking into consideration the states of nonequilibrium in the reacting combustion gas. The calculation scheme used explains the degrees of ionization observed and offers at the same time a key to the calculation of the preliminary stages of this ionization, that is, the chemiluminescence. On the other hand, the intensities of the reaction luminescence thus calculated clarify, in turn, the preparation processes in continuous burning.

The clarification of the questions raised here goes far beyond the field of rockets in its technical implication. It covers not only all types of reaction power plants and internal combustion engines, but also general technical heating units, the problems of powder combustion, of explosion and detonation phenomena, of gas kinetics at very high flight altitudes and flight velocities, of technical application of atomic energy, etc.

## II. ON THE DETERMINATION OF THE DEGREE OF IONIZATION BY REFLECTION MEASUREMENTS

The classic test methods for the determination of the degree of ionization of a flame by measuring the resistance between relatively cool electrodes have serious disadvantages since the aerodynamic and thermal boundary layers of finite thickness at the electrode surfaces with their low temperatures and adherent static boundary layers permit the establishment of the ionization equilibrium and then, as electrically insulating layers, completely blur the picture of gas conductivity, and therewith of ionization.

Probe test methods are therefore probably less suitable for the investigation of the validity of the Saha equation for flames than the method of measuring the ionization by reflection of short electrical waves; the latter method is largely free from disturbance of the state of the combustion gas by the measuring apparatus.

A series of tests (reference 1) showed the phenomenon that flames were able to reflect even very short electrical waves in the centimeter range and, under certain circumstances, even in the millimeter range with a reflection coefficient approaching metallic reflection. Due to the simple ray formation possibilities of such short waves, this phenomenon enables and suggests the determination of the maximum degree of ionization of a flame in a manner analogous to ionosphere measurements. Since the relations of the gas state differ from the ionosphere, it will be expedient to enumerate here the relations on which the measuring method for flames is based.

According to the theory of dispersion, the generally complex refractive index  $n$  of a medium with a magnetic permeability of  $\approx 1$  is, for an electrical wave of the angular frequency  $\omega = 2\pi f$ , a function of that frequency. The influence of the terrestrial magnetic field may be neglected in view of the high frequencies occurring in flame measurements; on the other hand, those frequencies usually lie so far below the natural-frequency domains of the molecules of the flame gases that their influence will not be considered here. In neglecting the field influences of neighboring molecules polarized by the electrical wave on the free electrons or ions, that is, for validity of the so-called Sellmeier theory,  $n$  obeys the relation

$$n^2 - 1 = 4\pi \sum \frac{N_h \frac{e_h^2}{m_h}}{-\omega^2 + j\omega v_h} \quad (1)$$

where  $e_h$  is the charge,  $m_h$  the mass,  $v_h$  the mean impact number per unit time with neutral molecules or atoms of an oscillator of the type  $h$ ;  $N_h$  is the volume density of the corresponding oscillator type, and

$j = \sqrt{-1}$  the imaginary unit vector.

Consideration of the influences of neighboring polarized molecules according to the theory of Lorentz-Lorenz leads to an expression proportional to  $\frac{n^2 - 1}{n^2 + 2}$ . Concerning the validity criteria of one theory or

the other, compare the literature (reference 4). Somewhat higher degrees of ionization (about 50 percent) are obtained from the measured values with the Lorentz theory than with the Sellmeier equation; however, these deviations are small compared to the differences, frequently amounting to several powers of ten, between the results of measurements and of calculations with the Saha equation. The measured degree of ionization on which the following deliberations are based will be the minimum amount resulting from the Sellmeier equation.

In a thermal ionization by combustion processes (not for nuclear reactions!) the probability of multiple ionizations is very small. In the proximity of the reaction zone of a flame, that is, at the locus of the maximum degree of ionization, the densities of the free electrons formed and of the positive ions are therefore about equal. Since an oscillator's influence on  $n$  is inversely proportional to its mass, the refractive index of that zone is determined practically only by the density of its free electrons, and the simplified relation

$$n^2 = 1 + 4\pi \frac{N \frac{e^2}{m}}{-\omega^2 + j\omega\nu} \quad (2)$$

is valid for that zone with the corresponding values for electrons.

Due to its higher velocity of diffusion and the recombination of the electrons occurring, accompanied by formation of negative molecules first preeminently by attachments to neutral molecules, the density of electrons decreases, with increasing distance from the reaction zone, considerably more rapidly than the density of ions so that the refractive index is then determined by the sum of the separate oscillator contributions according to equation (1).

We shall denote the quantity

$$\sqrt{4\pi N \frac{e^2}{m}} = \omega_0 \quad (3)$$

as the "characteristic frequency" of the medium. Once the latter has been determined by measurements, one may calculate from it (by substituting the corresponding numerical values in equation (3)) the density of electrons in the zone of maximum ionization as

$$N [\text{cm}^{-3}] = 3.15 \times 10^{-10} \omega_0^2 [\text{sec}^{-2}] \quad (4)$$

and the corresponding degree of ionization  $\alpha_i$  for equal densities of electrons and ions as

$$\alpha_i = \frac{2NkT}{p} = \frac{2.82 \times 10^{-22} NT [\text{OK}]}{p [\text{atm}]} \quad (5)$$

In equation (5),  $k$  signifies the Boltzmann constant,  $T$  the absolute temperature, and  $p$  the gas pressure.

Due to the low gas density existing in the ionosphere, one may there almost always neglect the influence on the refractive index exerted by the impact damping and, respectively, the mean impact number  $\nu$  per second of an oscillator with the neutral molecules or atoms of the medium. For flames, this neglect is not immediately admissible; thus its effect on the reflection properties will be investigated here in more detail.

With the phase factor  $\mu$  and the damping factor  $\kappa$ , there exists, according to definition, between the complex refraction index  $n$  and the complex dielectric constant  $\epsilon$  (absolute value  $|\epsilon|$ ) the relation

$$n^2 = (\mu + j\kappa)^2 = \epsilon \quad (6)$$

With the abbreviations

$$A = 1 - \frac{\omega_0^2}{\omega^2 + \nu^2}$$

and

$$B = \frac{\nu}{\omega} \frac{\omega_0^2}{\omega^2 + \nu^2}$$

one obtains for the Sellmeier relation

$$|n^2| = |\epsilon| = \sqrt{A^2 + B^2} \quad (7)$$

$$\mu = \sqrt{\frac{1}{2} (|\epsilon| + A)} \quad (8)$$

$$\kappa = \sqrt{\frac{1}{2} (|\epsilon| - A)} \quad (9)$$

and the equation for an electrical plane wave propagated in the medium along the path  $s$  after a lapse of time  $t$  therewith reads

$$\underline{E} = \underline{E}_0 e^{-\frac{\omega}{c} \kappa s} e^{j\omega \left(t - \frac{\mu}{c} s\right)} \quad (10)$$

$\underline{E}_0$  therein denotes the initial magnitude of the vector of the electric field strength, and  $e$  the base of the natural logarithm.

For the sake of simplicity, one will work in reflection measurements on flames with electrical waves of approximately vertical incidence to the flame axis. For the reflection coefficient  $R$ , that is, the ratio between incident and reflected energy of a wave impinging from air ( $n \approx 1$ ) on a homogeneous ionized gas layer, one obtains in that case

$$R = \left( \frac{\underline{E}}{\underline{E}_0} \right)^2 = \frac{(\mu - 1)^2 + \kappa^2}{(\mu + 1)^2 + \kappa^2} \quad (11)$$

In figure 1, the reflection coefficients calculated according to equation (11) are represented as a function of the relative frequency  $\frac{\omega}{\omega_0}$  with the relative impact number  $\frac{v}{\omega_0}$ . As one can see from this figure, the transition from the reflecting to the transmitting state is discontinuous only for the characteristic frequency  $\omega_0$  if, as for instance in the ionosphere, the influence of impact damping is insignificant. The characteristic frequency  $\omega_0$  is, in that case, identical with the so-called limiting frequency. The more the influence of impact damping increases, the smoother the transition from one state to the other, and the smaller the possibility of an accurate determination of  $\omega_0$  from a measured reflection curve  $R = f(\omega)$ .

Actually, of course, a flame is not a homogeneously ionized medium; on the contrary, the degree of ionization decreases, due to mixing, diffusion, and recombination, starting from the reaction zone, in the direction of the longitudinal flame axis as well as radially to it. Thus, waves impinging on the flame penetrate it, according to frequency, more or less deeply until they meet with the degree of ionization required for their reflection, being damped in the process according to equation (10). The calculation of such cases was treated for the ionosphere by Foersterling, Elias, Rayer, and Epstein, among others (references 5, 6, 7, 8).

For the case of flames, one must take into consideration in such calculations that the impact number also is to a very high degree and nonlinearly dependent on the path. A derivation of the relations for the reflection coefficient under assumption of the spatial distribution of the impact numbers and of the densities of electrons and ions, respectively, caused by the changes in temperatures and the intermixing, would exceed the scope of this report; thus, we shall only show in figure 2 the result of such a calculation for a wave which at a certain point impinges on a flame moving at supersonic velocity.

The characteristic course of these calculated curves shows good agreement with measured reflection curves particularly in the neighborhood of the characteristic frequency ( $\frac{\omega}{\omega_0} = 1$ ). In contrast, the measured curves showed for long waves, that is, high values of  $\frac{\omega_0}{\omega}$  again a decrease in reflecting power caused by refraction phenomena.

In most combustion processes, Maxwell-Boltzmann's velocity distribution largely applies for the free electrons. A degeneration of the electron gas in the direction of the Fermi statistics is to be expected only for the combustion of metals with low ionization energy. When the Maxwellian velocity distribution is valid, one may derive for the mean number per second of collisions of an electron with neutral molecules

the expression

$$v = \sqrt{8\pi/kT} \sum_{i=1}^n r_i^2 p_i \quad (12)$$

where  $k$  signifies the Boltzmann constant,  $T$  the absolute temperature,  $r_i$  the effective radius of a molecule of the gas component  $i$ , and  $p_i$  its partial pressure. For the derivation of equation (12), the mean velocity of an electron was assumed to be, due to the effect of the electrical wave, small compared to the mean heat velocity. It is advisable to work in reflection measurements with correspondingly low field strengths, since otherwise the impact frequency becomes nonlinearly dependent on the effective value of the alternating field. From the occurrence of the so-called Luxemburg effect (which is based on this fact), one may, on the other hand, approximately determine the mean impact number in a flame by experiment.

Besides being a function of the electron velocity, the effective radius  $r_i$  in equation (12) is also dependent on the degree of molecular excitation. In most combustion processes, a very accurate calculation of  $v$  is therefore not possible. Since, however, not the absolute value of  $\omega_0$  and  $N$ , respectively, is a function of  $v$ , but only the accuracy with which these values can be determined at a certain point of a flame, an estimate of the order of magnitude of  $v$  is sufficient for the present case. For this purpose, we may, for instance for a hydrocarbon combustion, by extrapolation from measurements of Ramsauer (reference 9), assume the effective radius of the molecules present in the flame as about 1.5 Å. For standard pressure, the electron impact numbers then lie, according to the temperature of the location considered, approximately between  $10^{10}$  and  $10^{11}$  per second.

The values of  $\omega_0$  experimentally determined in the reaction zone of such hydrocarbon flames were, according to the heating value of the fuel, of the order of magnitude of  $10^{10}$  to  $10^{12}$  per second, the corresponding electron densities between  $10^{11}$  and  $10^{14}$  cm<sup>-3</sup>.

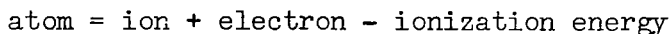
These numerical values show that the ratio  $\frac{v}{\omega_0}$  was still relatively small for most flames investigated. From the sharp transition for small values of  $\frac{v}{\omega_0}$  from the reflecting to the transmitting state,  $\omega_0$  and  $N$ , respectively, could then be determined with good accuracy from the reflection curve found experimentally, according to figure 2.

For decreasing temperature  $v$  increases, according to equation (12), in proportion to  $\sqrt{T}$ . The electron density decreases, for diminishing temperature, by recombination about proportionally to  $T^{3.5}$ . With distance from the reaction zone,  $\frac{v}{\omega_0}$  therefore increases very rapidly, and the accuracy of the reflection method is then reduced accordingly. However, for the determination of the maximum degree of ionization of a flame, this phenomenon is of lesser practical significance.

The validity of the theory of dispersion for ionized gases, largely confirmed by ionosphere research, makes it appear very improbable that the reflection measuring method which is based on it yields, for flames, degrees of ionization too high by orders of magnitude. Thus, the following section will be devoted to an investigation of how far the presuppositions for application of the Saha equation exist for flames.

### III. CALCULATION OF THE DEGREE OF IONIZATION OF FLAMES ACCORDING TO THE SAHA EQUATION

In case of perfect energy equilibrium, thermal ionization may (references 10 and 11) be interpreted as a chemical dissociation process according to the equation



assuming the number of electrons freed to be equal to the number of ions formed. This assumption is permissible in combustion processes for the reason that the energy for splitting off a second valence electron is so much greater than the one requisite for the first that the probability of multiple ionizations remains very small.

According to the law of mass effect, there exists between the equilibrium constant  $k_p$  and the degree of ionization  $\alpha_i$  of a chemically uniform gas the relation

$$k_p = \frac{f_{\text{ion}} p_{\text{ion}} f_{\text{el}} p_{\text{el}}}{p_{\text{atom}}} = f_{\text{ion}} f_{\text{el}} p \frac{\alpha_i^2}{1 - \alpha_i^2} \quad (13)$$

where  $p$  is the gas pressure and  $p_{\text{el}}$ ,  $p_{\text{ion}}$ , and  $p_{\text{atom}}$  are the partial pressures of the electrons, ions, and neutral particles of the ionizing mixture, respectively; furthermore,  $\alpha_i$  is the ratio of the number of ionized particles or, respectively, freed electrons (the number

of which is to equal that of the ions) to the number of neutral molecules originally present; and  $f_{ion}$  and  $f_{el}$ , respectively, signify so-called activation coefficients with which the concentrations or partial pressures must be multiplied for charge carriers so that the law of mass effect is preserved. They become equal to unity when the degree of ionization  $\alpha_i$  becomes zero, and drop to small values with increasing ionization.

On the other hand, one may derive from van t'Hoff's equation for the value of the equilibrium constant  $k_p$  as a function of the temperature, according to Eggert (reference 10), with accuracy sufficient for most purposes the relation

$$k_p = (kT)^{5/2} \left( 2\pi m_{el}/h^2 \right)^{3/2} e^{-w_o/kT}$$

$$= 1.43 \times 10^{57} (kT)^{2.5} e^{-w_o/kT} \quad (14)$$

where  $w_o$  signifies the ionization energy for the first valence electron per molecule  $[mkg]$ ,  $m_{el}$  the mass of an electron  $[kgs^2/m]$ ,  $k$  the Boltzmann constant  $[mkg/o]$ , and  $h$  Planck's energy quantum  $[mkgs]$ .

In deriving this equation, we made the following assumptions:

1. The thermodynamic constants for ion and neutral molecule were to be equal.
2. The electron was to correspond in its properties to a monatomic molecule of accordingly small molecular weight.
3. The dependence on the pressure of the equilibrium constant  $k_p$  above about  $p = 30$  atmospheres was to be neglected. (According to Eucken (reference 12) the value  $\log k_p$  decreases, for higher pressures, about linearly with the increasing pressure.)

From equations (13) and (14) and the further approximation assumption  $f_{ion}f_{el} = 1$ , there results the so-called Saha equation

$$\frac{\alpha_i^2}{1 - \alpha_i^2} = 1.43 \times 10^{57} \frac{(kT)^{2.5}}{p} e^{-w_o/kT} \quad (15)$$

or in the notation more familiar to the engineer

$$\frac{\alpha_i^2}{1 - \alpha_i^2} = \frac{4.73 \times 10^3 U_i^{5/2} e^{-1/\vartheta}}{p}$$

$$= \frac{B}{p} \vartheta^{5/2} e^{-1/\vartheta} \quad (16)$$

Therein:  $\vartheta = \frac{kT}{\epsilon U_i}$   $B = 4.73 \times 10^3 U_i^{5/2}$

$\epsilon$  = elementary charge in [AS]

$U_i$  = ionization energy in [eV]

$p$  = pressure in [kg/cm<sup>2</sup>]

For the types of molecules usually present in the flames investigated by reflection measuring methods, the values of the ionization energy  $U_i$  and of the constants  $\vartheta/T$  and  $B$  are compiled in the following table:

Type of gas	$U_i$	$(\vartheta/T) \times 10^6$	$B \times 10^{-6}$
$H_2O \rightleftharpoons H_2O^+ + e^-$	13.0	6.63	2.82
$CO_2 \rightleftharpoons O - C - O^+ + e^-$	14.4	5.98	3.74
$CO \rightleftharpoons CO^+ + e^-$	14.1	6.11	3.55
$OH \rightleftharpoons OH^+ + e^-$	11.6	7.43	2.16
$O_2 \rightleftharpoons O - O^+ + e^-$	12.5	6.90	2.60
$H_2 \rightleftharpoons H - H^+ + e^-$	15.8	5.45	4.73
$O \rightleftharpoons O^+ + e^-$	13.57	6.35	3.18
$H \rightleftharpoons H^+ + e^-$	13.54	6.36	3.14

With the aid of these values, the theoretical variation of the degree of ionization  $\alpha_i$  and of the electron concentration  $N'$  per cm<sup>3</sup> along a typical V2-rocket was plotted in figure 3 with the characteristic data

Cross section	$f_o$	$f'$	$f_m$ (at the bottom)
$\phi$ [m]	0.950	0.403	0.700
$p$ [atm]	16.7	9.25	1
$T$ [°K]	2820	2520	1605

and normal hydrocarbon-oxygen combustion, under the assumption of unconditional validity of the Saha equation in any cross section of the rocket. Accordingly, for instance, an electron density of  $0.08 \text{ cm}^{-3}$  results in the outlet cross section  $f_m$  at  $1605^\circ\text{K}$  gas temperature and 1 atmosphere pressure, a value which cannot explain the reflection of centimeter waves in the exhaust jet, since for that phenomenon electron densities of more than  $10^{11} \text{ cm}^{-3}$  are required. If one admits a certain inertia in the reformation of the ionization originated before and considers as the possible limiting case the maximum ionization development in the interior of the combustion chamber  $f_o$  at  $2820^\circ\text{K}$  and 16.7 atmospheres, the calculation of the electron density according to Saha yields for the interior of the chamber a value of  $3.3 \times 10^9 \text{ cm}^{-3}$  and with consideration of change in pressure and volume for constant degree of ionization  $\alpha_i$  in the outlet cross section  $f_m$  a value of  $N' = 3.5 \times 10^8 \text{ cm}^{-3}$ . From this maximum possible value, the losses due to recombination and electron diffusion on the way between reaction zone and test point have not yet been subtracted; and yet even that value would not suffice for explaining the centimeter waves reflection measured.

Before attempting a deeper explanation, we shall briefly estimate the possible influence of the neglected activity coefficients  $f$  on the calculation results. These quantities, in the Saha equation assumed to be equal to unity, actually are noticeably reduced with increasing ion concentration, so that if their true values were taken into consideration, the degree of ionization would have to increase more than corresponds to the classical Saha equation. The appearance of the activity coefficients is explained by the force effects between the electrically charged minute particles, and is therefore a function of the charge intensity of the ions, of the ion distance, and of the ion radius. Detailed measuring series with respect to concentration and theories of activity coefficients seem so far to be known only in the field of electrolyte solutions.<sup>1</sup> Here there applies, for instance, in the field of very diluted solutions according to Debye-Hueckel for single ionization, accompanied by formation of two oppositely charged ions, the formula  $\log f = -0.505 \sqrt{c_o}$  where  $c_o$  denotes the total concentration of the electrolyte mol/liter. The same mean ion distances as an electrolyte solution of the concentration  $c_o = 1 \text{ mol/liter}$  would have in gas plasma an ion concentration of  $\sim 6 \times 10^{20}$  particles per  $\text{cm}^3$ . If it were permissible to extend the regularities of electrolytes to gas plasmas, an ion concentration of  $10^{11} \text{ cm}^{-3}$ ,

<sup>1</sup>The improved formulas of Rosseland for calculation of the thermodynamic ionization, "Astrophysik auf atomtheoretischer Grundlage" (Astrophysics on an atom theoretical basis) Berlin, 1931, were, unfortunately, not accessible to the authors.

for instance, would correspond only approximately to  $2 \times 10^{-10}$  mol/lit, and would therefore not yet cause activity coefficients deviating noticeably from unity. However, all the ion and electron concentrations that have appeared so far in the calculation still lie below this value.

Thus, it seems plausible to look for the reason for the deviation of the measuring results from the values calculated according to the Saha equation in the fact that the presupposition for the validity of the Saha equation, namely that of a well-established state of equilibrium, was not satisfied in the case of the flames investigated; probably it does not, in general, occur for flames.

#### IV. CALCULATION OF THE DEGREE OF IONIZATION OF FLAMES FROM STATES OF NONEQUILIBRIUM

We shall now attempt to explain why the Saha equation, which is based on assumptions of equilibrium, probably cannot yield correct results for combustion phenomena using a schematic representation of a combustion process.

We assume for this purpose that in such a process by appropriate insulation the total amount of energy supplied by the heating value of the fuel is kept constant for the duration of the balancing of the equilibria of the different degrees of freedom, thus, that the process is adiabatic.

On the basis of the results of well-known research reports (references 13, 14, 15, 16, 17, 18, and 19, among others) one may assume for some estimates that the impact numbers required for establishment of thermal equilibrium are, after a considerable change of state of the gases:

For	Translation	Rotation	Vibration	Dissociation	Ionization
In the ratio of	$10^1$	$10^3$	$10^5$	$10^7$	$10^9$

The customary equilibrium relations, law of mass effect, Saha equation, etc., describe a state in which the same numbers of partners newly originate and vanish per unit time. Their application is justified only for gases in which at least  $10^7$  impacts per particle have taken place

since the change in state (for dissociation equilibria) or at least  $10^9$  impacts when ionization equilibria (under certain temperature conditions) are discussed.

For rockets, the time lags usually are sufficient for the establishment of the dissociation equilibria in the chamber; they are frequently insufficient for the establishment of dissociation for the nozzle flow (reference 3) and always insufficient by far for the establishment of ionization (reference 20).

One may visualize the processes leading to ionization by means of the following scheme which is still more modified by the mechanism of the chain reactions.

The initial state of the combustion gases, at any rate, is the state immediately after the chemical reaction where the total reaction energy  $E$  exists as undistributed translation and the molecular velocity of the particle just originated therefore is

$$C_1 = \sqrt{2gE/A} \quad (17)$$

where  $g$  denotes the acceleration of gravity and  $1/A$  the mechanical heat equivalent. A stoichiometric hydrocarbon-oxygen rocket has, for instance,  $E = 2587$  kcal/kg mixture heating value, thus,  $c_1 = 4640$  m/sec.

In view of the ionization energies  $\epsilon_i$  of the molecules appearing by hydrocarbon combustion in oxygen between 7750 and 11,000 kcal/kg which correspond to particle velocities of 8050 to 9600 meters per second, this first state cannot lead to ionization if translation impacts of molecules are assumed as the first cause for the formation of free electrons in a thermal ionization.

The first equilibrium adjustment occurring in the course of the first 10 impacts, according to the table above, will be that of the Maxwellian distribution of these pure translation energies. To this distribution there corresponds, according to Boltzmann, a translation temperature  $T_t$  of

$$T_t = \frac{2}{3} \frac{EM}{R} \quad (18)$$

where  $M$  is the molecular weight and  $R$  the general gas constant. For the example mentioned, this temperature amounts with  $M = 30$  kg/mol and  $R = 2$  kcal/mol degrees approximately to  $T_t = 10 E = 25,870^\circ\text{K}$ .

The mean particle velocity after the establishment of translation is

$$c_2 = c_1 = \sqrt{\frac{2gE}{A}} = \sqrt{\frac{3gRT_t}{MA}} \quad (19)$$

thus for our example again  $c_2 = c_1 = 4640$  meters per second.

In addition to this mean molecular velocity, there occur, as is well known, in the Maxwellian distribution of the second state all molecular velocities between 0 and  $\infty$ , therefore, also those above the ionization velocity  $c_i = 8050$  to 9600 meters per second of a not-excited particle.

The portion of weight formed by the gas particles  $N'$  which move more rapidly than at  $c_i$ , from which therefore under most favorable circumstances ionization could be expected, amounts for large  $c_i/c_1$  to approximately

$$\frac{N'}{N} = \sqrt{\frac{6}{\pi}} \frac{c_i}{c_1} e^{-\frac{3}{2} \left(\frac{c_i}{c_1}\right)^2} \quad (20)$$

for the example, therefore,  $N'/N = 0.6 \times 10^{-2}$ , for the combustion gases of the V2 with  $E = 1540$  kcal/kg,  $c_1 = 3590$  m/sec.,  $N'/N = 0.16 \times 10^{-3}$ .

The exact degree of ionization would therewith be known for 100 percent effectiveness of the few impacts at disposal. Thus, the energy portion contributed by the ionization would be for the rocket of the example 3.2 percent, for the V2 0.1 percent of the energy converted.

With further increasing impact number of the separate particles, the pure translation energy so far considered exclusively is distributed, according to the above table of impact numbers, between more and more degrees of freedom, with the Maxwellian velocity distribution always maintained, until after  $10^7$  impacts the known dissociation-equilibrium temperature is attained; thus, for the rocket of our example, with 100 atmospheres chamber pressure,  $T_3 = 3700$  °K, which corresponds to a mean molecular velocity of  $c_3 = \sqrt{3gRT/AM} = 1760$  meters per second. The weight portion of the gas particles now still more rapidly moving than at  $c_i$  is about  $N'/N = 3.5 \times 10^{-8}$  and approaches the values offered by the Saha equation.

During the processes of adjustment to the separate degrees of freedom, the portion of the translation velocity which exceeds the ionization velocity will be able to lead to ionization in every case (excluding photo ionization) until after about  $10^9$  impacts all equilibria are established and therewith also the equilibrium temperature is attained on which the Saha equation is based.

In figure 4, we made an attempt to represent the energy balance of this schematic course of a combustion process. From this figure, combined with equation (20), one can see that after the establishment of rotation equilibrium, the probability of further ionization impacts becomes vanishingly small. Thus, the large majority of all free electrons would have to be formed during the first  $10^3$  impacts after the reaction.

In case of prescribed flow velocity of the flame, the impact number, according to figure 4, also is a certain criterion for the distance of the particle considered from the reaction zone at which the establishment of the respective degree of freedom is to be expected. From the variation of temperature, pressure, and flow velocity as a function of the flow path, one obtains, for instance, the fact that a particle, on the average, can have undergone at most  $10^6$  impacts since the reaction has taken place. Accordingly, the Saha equation cannot yet be valid for this point because for it the presuppositions of an established equilibrium between ionization and recombination (for which here about  $10^9$  impacts are prerequisite) do not yet appear satisfied.

Equation (20) at first only indicates what portion  $N'$  of the total number of particles  $N$  may, after the establishment of translation equilibrium, lead to ionization.

To the same extent that translation energy is converted into ionization energy by ionization impacts, a continuous reestablishment of the Maxwellian distribution for the translation energy and replenishment of the consumed terminal region of fast-moving particles take place so that more and more new particles become capable of ionization until the sudden drop in the translation-energy level due to adjustment to rotation becomes noticeable. Thus, in the course of the first  $10^3$  impacts, a multiple of the number of particles expressed by equation (20) will attain the minimum energy required for ionization.

The free electrons formed, too, assume (at least for low degrees of ionization) an approximately Maxwellian velocity distribution so that then an ionization by electron impacts also is to be expected.

Due to cumulative excitation, that is, to impacts with already excited molecules, it is possible that for some impacts ionization may take place by means of a kinetic energy which is lower than the ionization energy from the basic state.

First, the probability for ionization resulting from these facts is considerably higher than indicated by the result of equation (20).

On the other hand, it is not to be expected that every impact of a particle with a kinetic energy exceeding the ionization energy actually

leads to an ionization. According to the energy and momentum theorem, for instance, in case of central nonelastic impact and approximately equal mass of the impact partners, the original kinetic energy of the colliding particles must equal double the ionization energy if ionization is to take place with the momentum maintained. According to the Maxwellian distribution, the portion of particles with double ionization velocity is only a very small fraction ( $\approx 10^{-8}$ ) of the particles according to equation (20). For electron impacts, in contrast, the single ionization energy is a sufficient presupposition due to the large difference in masses.

Computational consideration of all these processes offers great difficulties even for the simplest combustion processes such as, for instance, hydrogen combustion. For the combustion of hydrocarbons, one has to cope with the added difficulty that the course of the individual, highly complicated chain reactions is not yet known sufficiently.

If one takes equation (20) as basis for the calculation of the maximum degree of ionization of a flame, that is, the degree of ionization of the reaction zone, and takes all the processes mentioned (which, however, so far have defied individual computation) into consideration by means of an additional "effectiveness factor," this factor lies, depending on the type of fuel, in the order of magnitude of several percents in order to bring about agreement between calculation and measurement. It is a value which approximately agrees with the impact utilization factors in electrical gas discharges.

So far, the authors have been prevented from a more accurate experimental determination of the utilization factor by lack of test installations.

Ionization depends therefore, first of all, only on the mixture heating value  $E$  of the fuel, not, however, on the operating conditions of the rocket, for instance, chamber pressure, state of expansion, or the like. These results also agree fundamentally with measurements of the reflecting power of the exhaust jets for centimeter waves made by one of the authors, which led to electron concentrations dependent on the heating value of the fuels and independent of the chamber pressures between 150 atmospheres and 1 atmosphere, and make the conception of combustion gas behavior deduced above seem highly probable.

## V. CALCULATION OF THE CHEMILUMINESCENCE OF FLAMES FROM STATES OF NONEQUILIBRIUM

The agreement with respect to order of magnitude between the ionization thus calculated and the values measured with the aid of radio principles encourages application of the same mechanism for calculation of the chemiluminescence.

All impacts of the Maxwellian distribution of the pure translation equilibrium in the second state which occur more slowly than at ionization velocity will obviously lead only to excitation of radiation since not a sufficient number of impacts took place to permit the establishment of rotation-oscillation dissociation. In case of electron excitation, the excitation fades, as is well known, after about  $10^{-8}$  second, that is, for our example after about  $10^3$  impacts with simultaneous emission of light, if it was not damped before by impacts of the second kind.

Whereas the equilibrium radiation of combustion gases takes place preeminently in the infrared long-wave region, the chemiluminescence of the type considered occurs in the short-wave region with wave lengths up to, at most, the beginning of the infrared spectral region ( $O_2$ -lines to  $4000 \text{ \AA}$ ) which corresponds to minimum energies of approximately 2390 kcal/kg or impact velocities of  $c_e = 4470$  meters per second.

The portion of molecules of state 2 which is of importance for luminescence lies, therefore, in the velocity range between  $c_e = 4470$  meters per second and  $c_i = 9150$  meters per second and amounts to

$$\xi = \frac{N_e}{N} = \sqrt{\frac{6}{\pi}} \left\{ \frac{c_e}{c_1} e^{-\frac{3}{2} \left( \frac{c_e}{c_1} \right)^2} - \frac{c_e}{c_1} e^{-\frac{3}{2} \left( \frac{c_i}{c_1} \right)^2} \right\} + \frac{2}{\sqrt{\pi}} \int_{x=\sqrt{\frac{3}{2}} \frac{c_e}{c_1}}^{\sqrt{\frac{3}{2}} \frac{c_i}{c_1}} e^{-x^2} dx \quad (21)$$

Thus, in our numerical example of the hydrocarbon-oxygen rocket,  $N_e/N = 0.42$ , thus, 42 percent of the reaction mass in the burner or the energy radiation  $0.42 \times 2390/2587 = 38.8$  percent of its energy output

when all molecules concerned actually come to radiate and show a lower radiation limit at 4000 ÅE.

The time between two impacts is, in practice, usually shorter than the life time of an excitation of

$$\tau = \frac{3cm}{8\pi^2 e^2} \frac{1}{\nu^2} = 45000 \lambda^2 \quad (22)$$

where  $c$  is the velocity of light,  $m$  the electron rest mass,  $e$  the elementary charge,  $\nu$  the frequency, and  $\lambda$  the wave length in meters.

Thus, a particle may radiate the frequency considered  $\nu = c/\lambda$  continuously in the limiting case. Therewith a simple transition is found from the radiation quantum  $\epsilon = h\nu$  to the radiation intensity  $J_0$ , if the optically effective molecular cross section  $Q = \pi r_0^2$  is introduced.

$$J_0 = \epsilon/Q\tau \quad (23)$$

If the molecule radiates simultaneously by means of a larger number of further excitation impacts, the intensity may become higher by one or two powers of ten; on the other hand, it may diminish by similar orders of magnitude due to the effectiveness factor discussed under ionization, so that one will be inclined to calculate at first with the simple relation (21). The results are, with the figures of our example

$$\epsilon = 5.07 \times 10^{20} \text{ mkg}, \quad Q = 5 \times 10^{-23} \text{ m}^2, \quad \tau = 0.72 \times 10^{-8} \text{ sec.}$$

$$\text{one } J_0 = 1.41 \times 10^{11} \text{ mkg/m}^2 \text{ sec} = 1.19 \times 10^{12} \text{ kcal/m}^2$$

that is, about  $10^5$  times more than would correspond to the black-body radiation in the total equilibrium at  $T = 3700^\circ\text{K}$ .

If, for instance, the known total luminescence per second of a big-scale high-pressure burner of 853,000 kcal/sec. energy output is  $0.388 \times 853,000 = 3.3 \times 10^5$  kcal/sec. luminescence radiation, and is with all this intensity visualized as combined on one surface, the magnitude of this surface is only

$$\frac{3.3 \times 10^5}{2.38 \times 10^8} = 1.4 \times 10^{-3} \text{ meters}^2$$

thus, for instance, a sphere of about 4.2 centimeters diameter.

The radiation of this sphere is absorbed in its proximity by all atoms and molecules present with an effective molecular radius of about  $r_0 = 0.4 \times 10^{-11}$  meters, a number of particles of  $n = 1.92 \times 10^{26} \text{ m}^{-3}$ , therefore an absorption constant  $a = nr_0^2 \pi = 0.96 \times 10^4 \text{ m}^{-1}$ . Thus, it diminishes, according to the absorption law  $J/J_0 = 1 - e^{-ar}$ , extremely rapidly with the distance  $r$  from the surface of that radiation center and becomes even at distances of millimeters weaker than the equilibrium radiation of carbon dioxide and water vapor.

Thus, the combustion gas is completely impervious to the locally concentrated, short-wave luminescence radiation; it can endanger a burner wall only in case of direct contact, which corresponds to the practical experience that the reaction zones of combustion gases are to be placed in the interior of the burner, as far away from the burner walls as possible. The dangerousness of luminescent gas particles near the walls of a high-pressure burner is, of course, greatly moderated in practice by flow and temperature boundary layers.

The extraordinary radiation opaqueness of the high-pressure combustion gas hardly allows, in practice, noticeable amounts of chemiluminescence to penetrate to the outside, rather it uses them like the high gas temperatures of the kinetic states 1 and 2 only for quick establishment of the energy equilibria, that is, it furthers this molecular impact process still more by photon impacts.

In burners of this type, the extraordinary intensity of the chemiluminescence causes very rapid vaporization of the injected fuel droplets even for the smallest path lengths and explains readily the rapid mixing in liquid-fuel rockets.

It must finally be noted that in burners of very low combustion-gas density, for instance, in those of ram jet engines, the absorption coefficients may be lower by several orders of magnitude than in the present example, making the combustion gas luminescence radiation opaque so that the latter starts contributing noticeably toward the heating up of the walls, as is well known from practical experience. In that case, the droplets of the fuels injected are then also noticeably heated up over larger distances. If it is, besides, a matter of combustion with air, the intensity of the luminescence itself is reduced very considerably, for instance from the value calculated before  $1.19 \times 10^{12} \text{ kcal/m}^2 \text{ h}$  to about  $7 \times 10^9 \text{ kcal/m}^2 \text{ h}$ , but remains nevertheless higher by more than four powers of ten than the pertaining equilibrium radiation of water vapor carbon dioxide. (Compare also 2.)

## CONCLUDING NOTE

The present hypothesis concerning origin and computability of ionization and luminescence in flames represents, altogether, not more than a quite preliminary attempt to give an explanation and quantitative comprehension of these phenomena so that the numerical data, in particular, may still have to be subjected to very extensive corrections. The authors are perfectly aware that some of their assumptions are rather daring and that further classification of the separate processes by additional experimental investigations is called for. Since the authors lack, however, at present the possibility of such experimental investigations, they deem it right to submit their opinions, confirmed as they are only by scanty observations, to scientific publicity in order to stimulate, perhaps, further observations and experiments.

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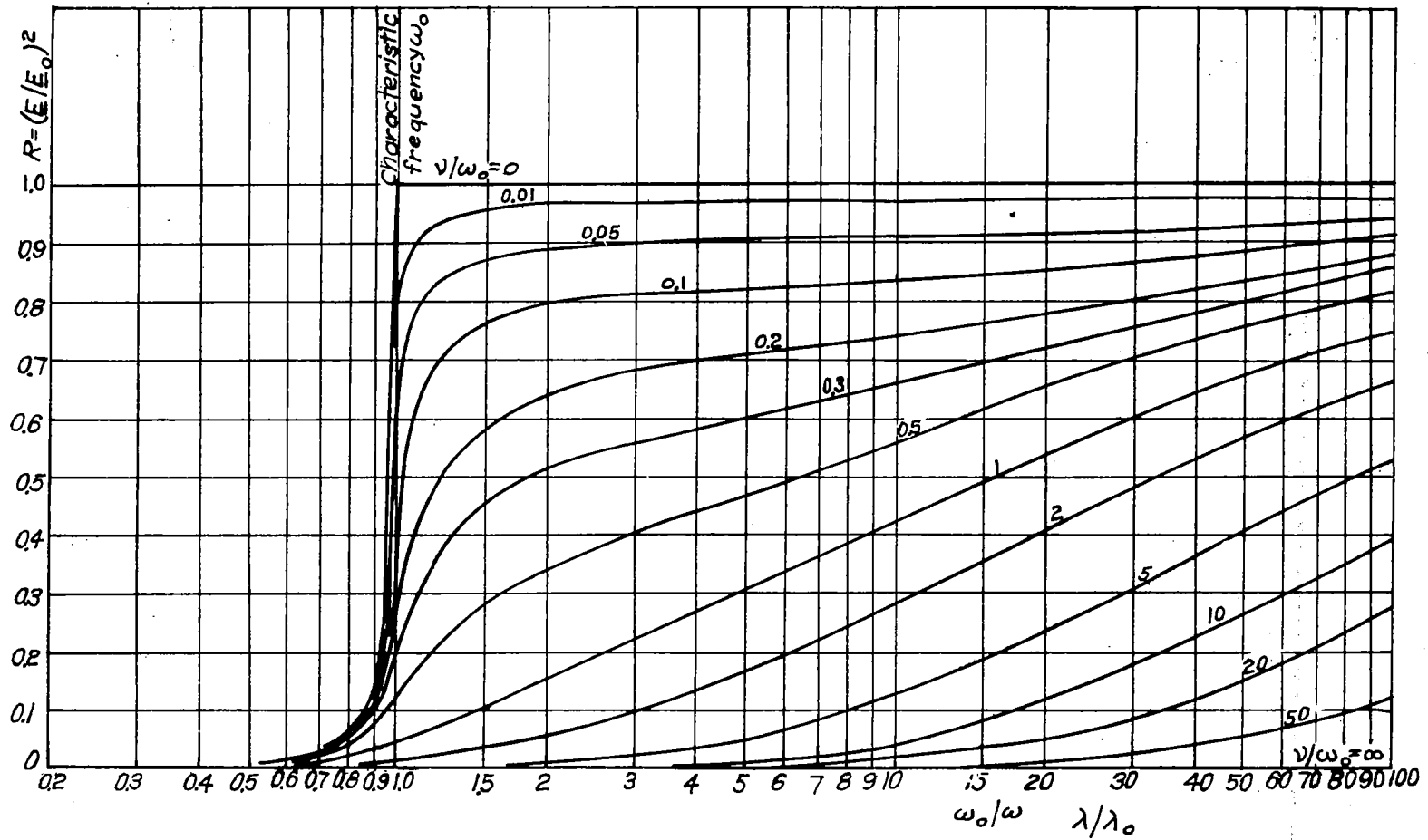


Figure 1.- Reflecting power  $R$  of a homogeneous ionized gas layer plotted against the relative frequencies  $\frac{\omega_0}{\omega}$  or wave lengths  $\frac{\lambda}{\lambda_0}$  with the relative impact number  $\frac{\nu}{\omega_0}$  as parameter.

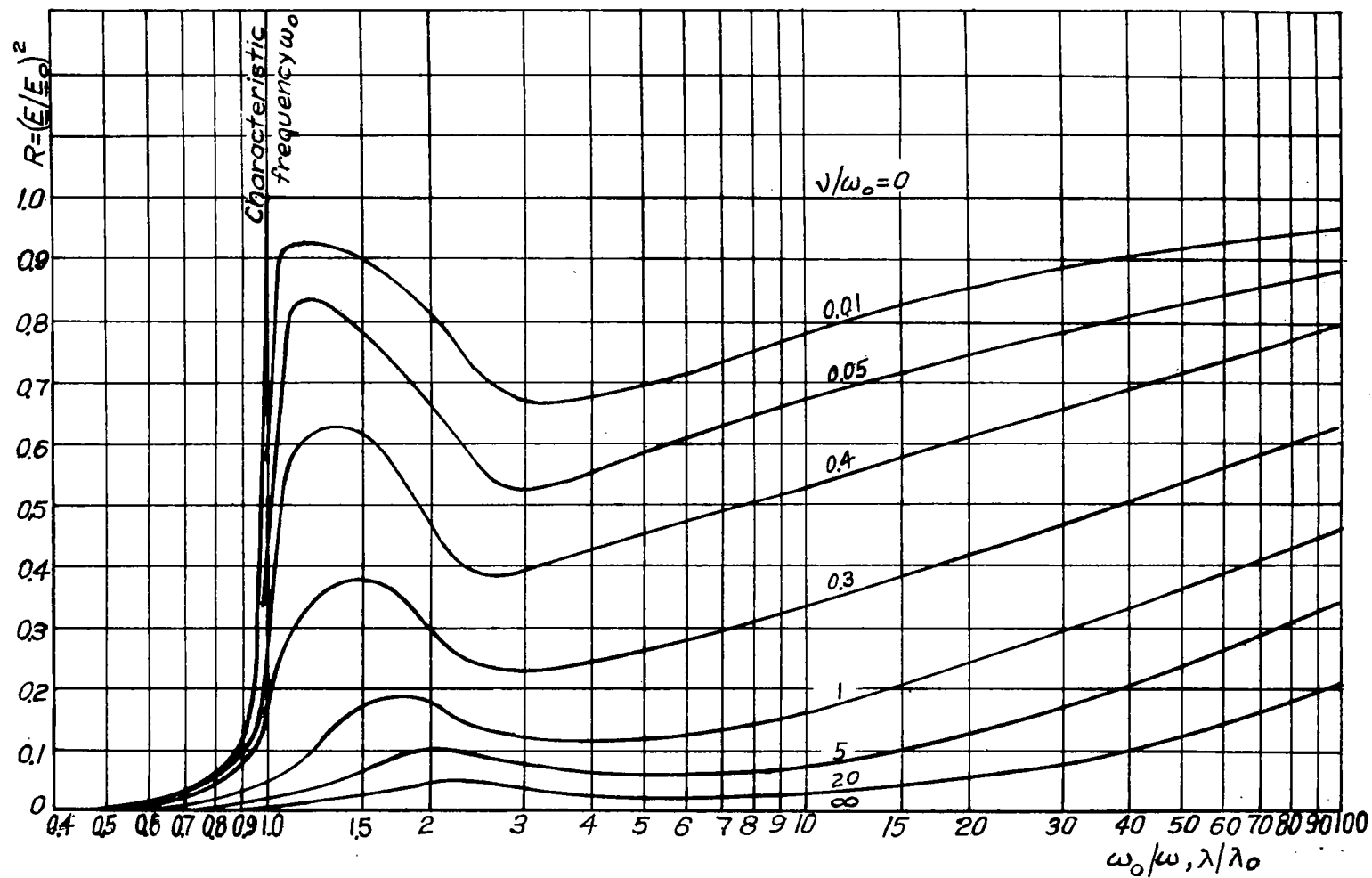


Figure 2.- Reflecting power of a gas column for a thickness of the mixing zone  $s_m = \lambda_0/10$  (distance from the nozzle opening  $l = 5.7\lambda_0$ ), relative impact number of the unmixed zone  $\frac{v}{\omega_0}$  as parameter.

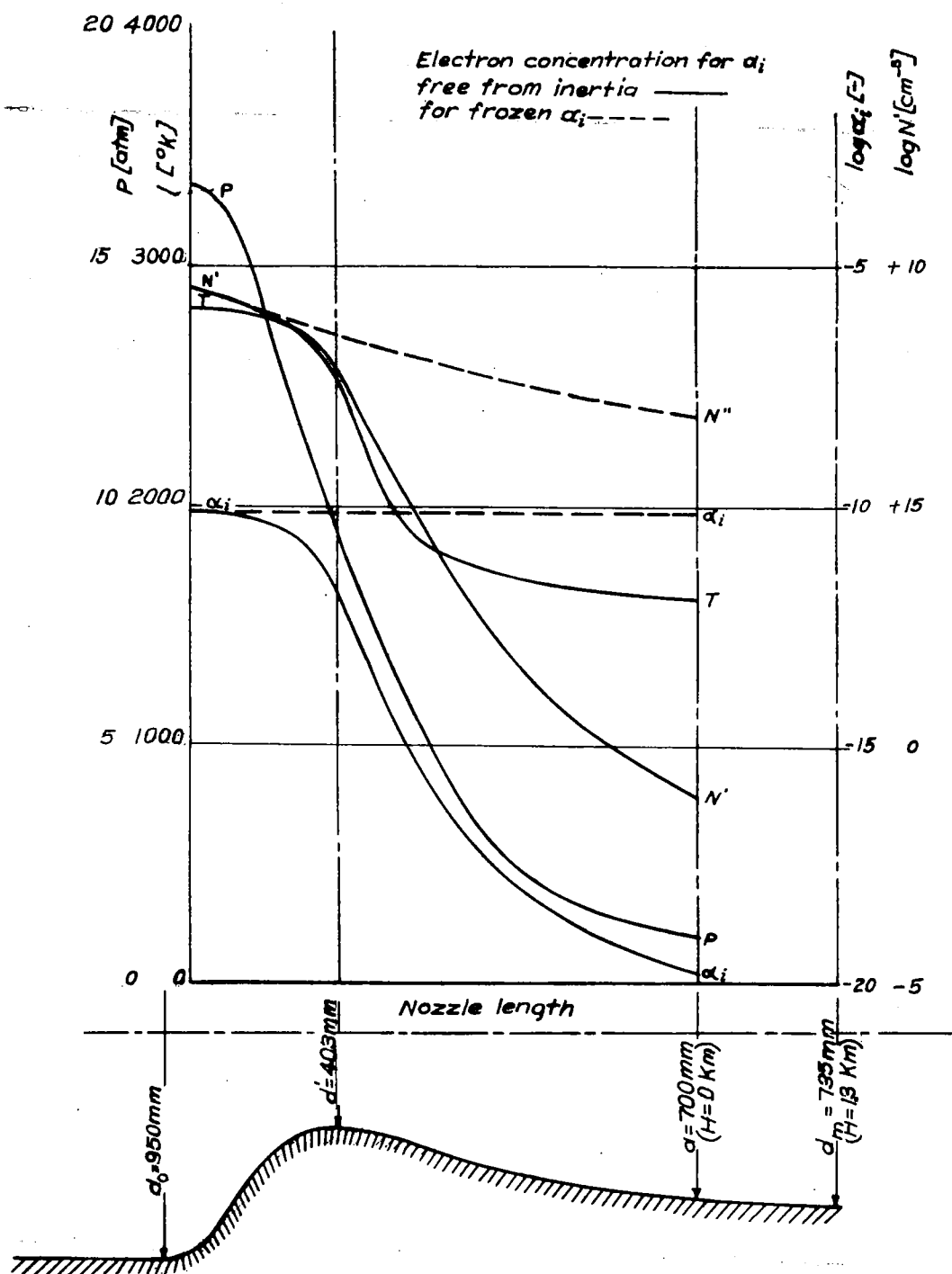


Figure 3.- Variation of temperature  $T$ , pressure  $p$ , degree of ionization  $\alpha_i$ , and number of electrons per centimeter<sup>3</sup>  $N'$  for a rocket similar to a V2 under assumption of the validity of the Saha equation.

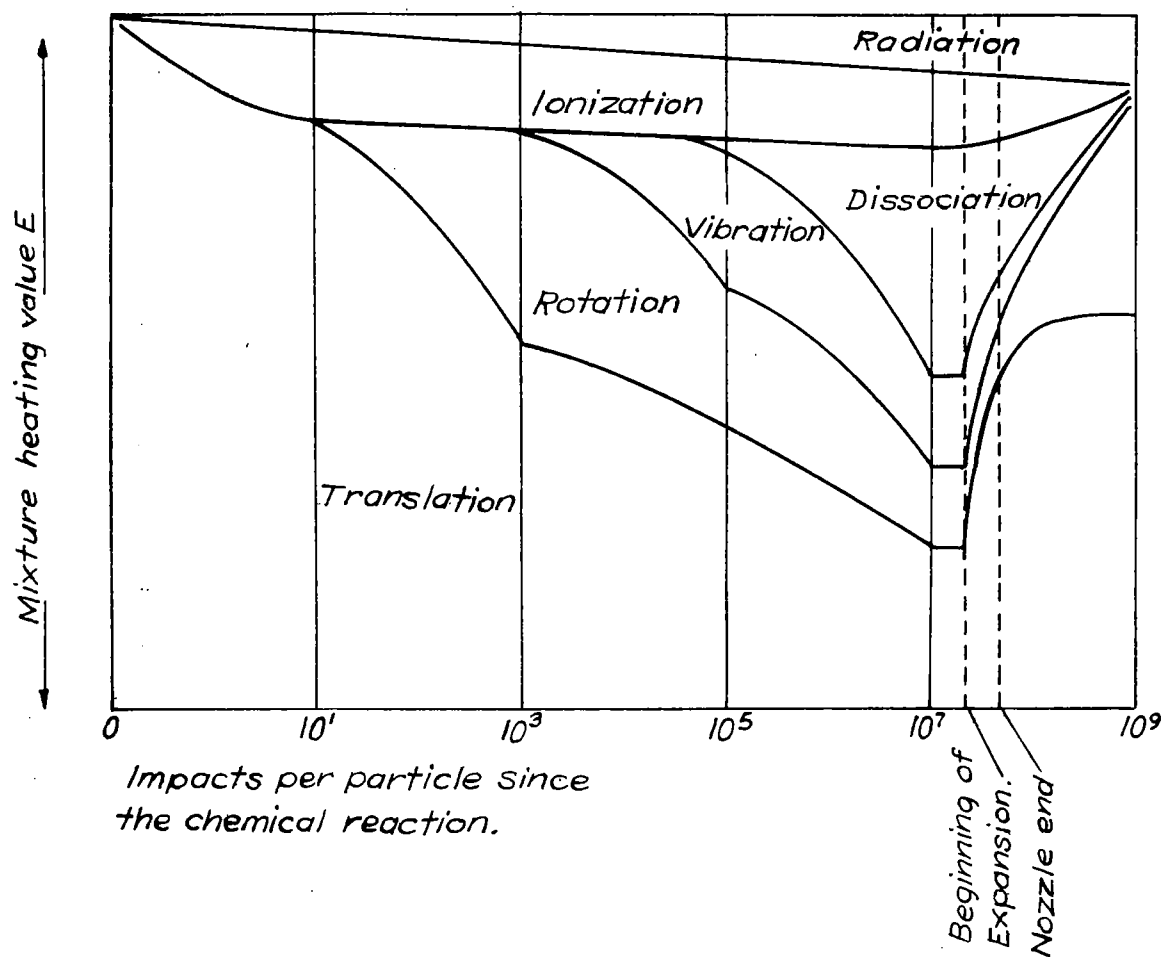


Figure 4.- Schematic course of equilibrium adjustments in the combustion gases of rockets.

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